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ALUMINIDE BOND COAT FOR A THERMAL BARRIER  
COATING SYSTEM AND METHOD THEREFOR

FIELD OF THE INVENTION

This invention relates to protective coating systems for components exposed to high temperatures, such as the hostile thermal environment of a gas turbine engine. More particularly, this invention is directed to a thermal barrier coating (TBC) system with an aluminide bond coat whose grain structure is modified to improve the spallation resistance of the TBC system.

BACKGROUND OF THE INVENTION

Higher operating temperatures for gas turbine engines are continuously sought in order to increase their efficiency. However, as operating temperatures increase, the high temperature durability of the components of the engine must correspondingly increase. Significant advances in high temperature capabilities have been achieved through the formulation of nickel and cobalt-base superalloys. Nonetheless, when used to form components of the turbine, combustor and augmentor sections of a gas turbine engine, such alloys alone are often susceptible to damage by oxidation and hot corrosion attack and may not retain adequate mechanical properties. For this reason, these components are often protected by an environmental and/or thermal-insulating coating, the latter of which is termed a thermal barrier coating (TBC) system. Ceramic materials and particularly yttria-stabilized zirconia (YSZ) are widely used as a thermal barrier coating (TBC), or topcoat, of TBC systems used on gas turbine engine components. TBC employed in the highest temperature regions of gas turbine engines is typically deposited by electron beam physical vapor deposition (EBPVD) techniques which yield a columnar

grain structure that is able to expand and contract without causing damaging stresses that lead to spallation.

To be effective, TBC systems must have low thermal conductivity, strongly adhere to the article, and remain adherent throughout many heating and cooling cycles. The latter requirement is particularly demanding due to the different coefficients of thermal expansion between ceramic topcoat materials and the superalloy substrates they protect. To promote adhesion and extend the service life of a TBC system, an oxidation-resistant bond coat is often employed. Bond coats are typically in the form of overlay coatings such as MCrAlX (where M is iron, cobalt and/or nickel, and X is yttrium or another rare earth element), or diffusion aluminide coatings. A notable example of a diffusion aluminide bond coat contains platinum aluminide (Ni(Pt)Al) intermetallic. When a bond coat is applied, a zone of chemical interaction occurs within the surface of the superalloy substrate beneath the coating. This zone is typically referred to as a diffusion zone (DZ), and results from the interdiffusion between the coating and substrate. The diffusion zone beneath an overlay bond coat is typically much thinner than the diffusion zone beneath a diffusion bond coat.

During the deposition of the ceramic TBC and subsequent exposures to high temperatures, such as during engine operation, bond coats of the type described above form a tightly adherent alumina ( $\text{Al}_2\text{O}_3$ ) layer or scale that adheres the TBC to the bond coat. The service life of a TBC system is typically limited by a spallation event brought on by thermal fatigue. Spallation of TBC deposited on MCrAlX bond coats generally occurs within the TBC near the TBC-to-alumina interface, while TBC

deposited on diffusion aluminide bond coats typically spall at the alumina-to-bond coat interface or within the alumina layer itself. As a result, the alumina-to-bond coat interface is particularly critical for TBC systems that employ diffusion aluminide bond coats.

In view of the above, it can be appreciated that bond coats have a considerable effect on the spallation resistance of the TBC, and therefore TBC system life. Consequently, improvements in TBC life have been continuously sought, often through modifications to the chemistries of the bond coat. The effect of the surface finish of MCrAlY bond coats has also been investigated, as evidenced by U.S. Patent No. 4,414,249 to Ulion et al. The results of this investigation showed that the service life of a columnar TBC can be improved by polishing an MCrAlY bond coat before depositing the TBC. The benefit of improving the surface finish of an MCrAlY bond coat is believed to be that a smoother alumina layer grows, which in turn provides a more uniform surface upon which the columnar TBC is deposited. The initial portion of a columnar TBC consists of many small grains that appear to grow in a competitive fashion, by which more favorably oriented grains eventually dominate less favorably oriented grains. By polishing an MCrAlY bond coat, it is believed that Ulion et al. reduced the number of nucleated grains, thereby reducing growth competition and improving the quality of the TBC adjacent the alumina scale, i.e., in the very region that TBC spallation tends to occur on an MCrAlY bond coat. According to Ulion et al., an optional additional treatment is to dry glass bead peen an MCrAlY bond coat to densify any voids and improve the coating structure.

As noted above, TBC spallation initiates by a

different mechanism on diffusion aluminide bond coats, and primarily along the alumina-bond coat interface. Accordingly, the toughness of the alumina and the alumina-bond coat interface are most important to TBC deposited on a diffusion aluminide bond coat. From this perspective, polishing a diffusion aluminide bond coat would be expected to reduce TBC life, since sufficient surface roughness of the bond coat would be desired to promote adhesion of the alumina to the bond coat, and to inhibit crack propagation through the alumina and alumina-bond coat interface. As a result, conventional practice has been to grit blast the surface of a diffusion aluminide bond coat to increase its roughness to about 50 microinches (about 1.25 micrometers) Ra or more before depositing the TBC.

#### BRIEF SUMMARY OF THE INVENTION

The present invention generally provides an aluminide bond coat for a thermal barrier coating (TBC) system and a method for modifying the grain structure of the aluminide bond coat in order to improve the thermal fatigue life of the coating system. The bond coat can be a single-phase  $[(\text{Ni}, \text{Pt})\text{Al}]$  or two-phase  $[\text{PtAl}_2 + (\text{Ni}, \text{Pt})\text{Al}]$  diffusion aluminide, though it is believed that overlay aluminide bond coats can also benefit from the teachings of this invention. The invention is particularly directed to aluminide bond coats deposited by methods that produce a generally columnar grain structure, in which grains extend through the additive layer of the bond coat, i.e., from the diffusion zone beneath the additive layer to the bond coat surface, such that grain boundaries are exposed at the bond coat surface. Two widely-used methods that produce bond coats of this character are vapor phase aluminizing (VPA) and chemical vapor deposition (CVD).

According to the invention, an aluminide bond coat having generally columnar grains is recrystallized to eliminate the original grain boundaries throughout the bond coat or at least adjacent the bond coat surface. In so doing, more stable (preferably equiaxial) grains are created at the bond coat surface where the critical alumina-bond coat interface will exist following oxidation of the bond coat and/or deposition of TBC on the bond coat. In addition, the original surface texture of the bond coat is altered to be smoother where grain boundaries meet the bond coat surface, and the diffusion zone of the bond coat may be modified so that refractory phases originally present at the interface between the additive layer and diffusion zone of the bond coat are no longer at the grain boundaries.

The method of this invention generally entails depositing the columnar aluminide bond coat on a superalloy component, and then cold working and heat treating the bond coat so that at least the surface portion of the bond coat is recrystallized. According to one embodiment of the invention, the bond coat is peened with sufficient intensity to cause recrystallization of at least the surface of the bond coat when sufficiently heated, such as during an appropriate heat treatment or during deposition of the TBC. The effect of recrystallization is that new and preferably equiaxed grains form at the bond coat surface, replacing the original columnar grains. Also within the scope of the invention are triangular and columnar grains that form at the bond coat surface as a result of recrystallization.

According to this invention, the original columnar grains of an as-deposited aluminide bond coat were found to be prone to accelerated oxidation at their grain boundaries, with oxidation initiating in the grain

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boundaries at the bond coat surface. Unexpectedly, the grain boundaries of recrystallized grains were shown to be much less prone to accelerated oxidation than the original grain boundaries. It is theorized that a lower oxidation rate at the grain boundaries eliminates a cause for the creation of initiation sites for localized creep and stress concentration at the bond coat surface, which are believed to cause the alumina layer to convolute and fracture. By eliminating or at least inhibiting the formation of sites where deformation of the alumina layer occurs, and thus where a fracture ultimately initiates and develops with thermal cycling, the spallation life of the TBC adhered by the bond coat is significantly increased. Another possibility is that the modified bond coat grain configuration exhibits more stable surface tension conditions, which slows a thermal grooving effect, that is, a tendency for the formation of valleys between adjacent grains.

Other objects and advantages of this invention will be better appreciated from the following detailed description.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a perspective view of a high pressure turbine blade.

Figure 2 is a cross-sectional representation of a TBC system on a surface region of the blade of Figure 1 along line 2--2.

Figures 3 through 5 show the progression of a spallation event of the TBC system of Figure 2.

Figure 6 is a cross-sectional representation of a TBC system with a diffusion aluminide bond coat exhibiting random recrystallization initiated at grain

boundary tips at the bond coat surface.

Figure 7 is a cross-sectional representation of a TBC system with an aluminide bond coat that has been fully recrystallized to yield equiaxial grains in accordance with a first embodiment of this invention.

Figure 8 is a cross-sectional representation of a TBC system with an aluminide bond coat whose surface region has been recrystallized to yield equiaxial grains limited to the surface region in accordance with a second embodiment of this invention.

Figure 9 is a cross-sectional representation of a TBC system with a single-phase aluminide bond coat that has been fully recrystallized with consequential grain growth in accordance with a third embodiment of this invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is generally applicable to components that operate within environments characterized by relatively high temperatures, and are therefore subjected to severe thermal stresses and thermal cycling. Notable examples of such components include the high and low pressure turbine nozzles and blades, shrouds, combustor liners and augmentor hardware of gas turbine engines. An example of a high pressure turbine blade 10 is shown in Figure 1. The blade 10 generally includes an airfoil 12 against which hot combustion gases are directed during operation of the gas turbine engine, and whose surface is therefore subjected to severe attack by oxidation, corrosion and erosion. The airfoil 12 is anchored to a turbine disk (not shown) with a dovetail 14 formed on a root section 16 of the blade 10. Cooling holes 18 are present in the airfoil 12

through which bleed air is forced to transfer heat from the blade 10. While the advantages of this invention will be described with reference to the high pressure turbine blade 10 shown in Figure 1, the teachings of this invention are generally applicable to any component on which a TBC system may be used to protect the component from its environment.

Represented in Figure 2 is a thermal barrier coating (TBC) system 20 of a type known in the art. As shown, the coating system 20 includes a bond coat 24 overlying a superalloy substrate 22, which is typically the base material of the blade 10. Suitable materials for the substrate 22 (and therefore the blade 10) include equiaxed, directionally-solidified and single-crystal nickel and cobalt-base superalloys. The bond coat 24 is shown as adhering a thermal-insulating ceramic layer 26, or TBC, to the substrate 22. As shown, the ceramic layer 26 has a strain-tolerant columnar grain structure achieved by depositing the ceramic layer 26 using physical vapor deposition techniques known in the art, particularly electron beam physical vapor deposition (EBPVD). A preferred material for the ceramic layer 26 is an yttria-stabilized zirconia (YSZ), a preferred composition being about 4 to about 8 weight percent yttria, though other ceramic materials could be used, such as yttria, nonstabilized zirconia, or zirconia stabilized by magnesia, ceria, scandia or other oxides. The ceramic layer 26 is deposited to a thickness that is sufficient to provide the required thermal protection for the underlying substrate 22 and blade 10, generally on the order of about 75 to about 300 micrometers.

The bond coat 24 is shown as being a diffusion aluminide of a type known in the art. The bond coat 24 is shown as being composed of an additive layer 28



overlying the substrate 22 and a diffusion zone 30 within the surface of the substrate 22. The diffusion zone (DZ) 30 contains various intermetallic and metastable phases that form during the coating reaction as a result of diffusional gradients and changes in elemental solubility in the local region of the substrate 22. The additive layer 28 is typically about 50 to 75 micrometers thick and contains the environmentally-resistant intermetallic phase MAI, where M is iron, nickel or cobalt, depending on the substrate material (mainly  $\beta$ (NiAl) if the substrate is Ni-base). The chemistry of the additive layer 28 is modified by the presence in the aluminum-containing composition of additional elements, such as chromium, silicon, platinum, rhodium, hafnium, yttrium and zirconium. For example, if platinum is deposited on the substrate 22 prior to aluminizing, the additive layer 28 consists of (Pt)NiAl-type intermetallic phases. The bond coat may be a single-phase [(Ni,Pt)Al] or two-phase [PtAl<sub>2</sub>+(Ni,Pt)Al] diffusion aluminide.

The bond coat 24 is represented in Figure 2 as being in an as-deposited condition, i.e., without any additional treatment provided by the present invention. In the as-deposited condition, the additive layer 28 is characterized by grains 32 that extend from the diffusion zone 30 to the surface of the bond coat 24, so that the grains 32 are generally columnar. As also represented, the grains 32 have grain boundaries 34 that intersect the surface of the bond coat 24 at an angle approximately normal to the surface. Those portions of the grain boundaries 34 parallel to the bond coat surface and bordering the diffusion zone 30 are shown as being decorated (pinned) with refractory phases 46 formed during deposition of the bond coat 24 as a result of diffusion of refractory elements from the superalloy substrate 22. Finally, the surface of the bond coat 24

is characterized by surface irregularities, termed grain boundary ridges, that correspond to the locations of the grain boundaries 34. The type of microstructure represented in Figure 2 is typical of aluminide bond coats deposited by chemical vapor deposition (CVD) and vapor phase deposition, e.g., vapor phase aluminizing (VPA).

As depicted in Figure 3, the aluminum-rich bond coat 24 naturally develops an aluminum oxide (alumina) scale 36 when exposed to an oxidizing atmosphere, such as during high temperature exposures in air. As portrayed in Figures 3 and 4, the oxide scale 36 is convoluted, with valleys 38 present above a majority of the grain boundaries 34 at the bond coat surface. During engine service temperature exposure, the oxide scale 36 continues to grow beneath the permeable ceramic layer 26. Failure of the TBC system 20 during engine service exposure typically occurs by spallation of the ceramic layer 26 from cracks that initiate in the oxide scale 36 and then propagate into the interface between the bond coat 24 and oxide scale 36. Consequently, the strength of this interface, stresses within the interface plane, and changes with temperature exposure influence the life of the TBC system 20.

During an investigation leading to this invention, superalloy specimens were coated with a TBC system of the type shown in Figure 2. The superalloys were Rene' N5 with a nominal composition in weight percent of Ni-7.5Co-7.0Cr-6.5Ta-6.2Al-5.0W-3.0Re-1.5Mo-0.15Hf-0.05C-0.004B-0.01Y, and Rene' R142 with a nominal composition in weight percent of Ni-12Co-6.8Cr-6.35Ta-6.15Al-4.9W-2.8Re-1.5Mo-1.5Hf-0.12C-0.015B. The ceramic topcoat was YSZ deposited by EBPVD, while the bond coats were single and two-phase PtAl deposited by VPA or CVD.



initiated and developed at some of the grain boundary tips, as represented in Figure 6. The result was the formation of triangular-shaped grains 42 at the bond coat surface. Due to their small size, these "new" grains 42 quickly transformed into the gamma prime phase. It was speculated that recrystallization was caused by either internal growth stresses in the bond coat or surface tension at the grain boundary tips. Unexpectedly, the new grain boundaries 44 did not appear to be susceptible to the accelerated oxidation exhibited by the original grain boundaries 34, nor did convolution of the oxide scale appear to initiate at the new grain boundaries 44. Furthermore, the original grain boundaries 34 appeared to be different from the new grain boundaries 44, in that the original boundaries 34 were somewhat indistinct when viewed in an SEM backscatter image, whereas the new grain boundaries 44 were always straight and well defined. This suggested a difference in microstructures and properties. Another significant observation was that all original grain boundaries 34 were decorated with tantalum-rich phases. Surprisingly, when an original grain boundary 34 was replaced by a new grain boundary 44, no tantalum-rich phases 46 (or other refractory phases) were found in the new boundary 44. It was therefore concluded that certain properties or characteristics of the original and newly formed grain boundaries 34 and 44 were different, and that these differences affected the susceptibility of an aluminide bond coat to oxidation and development of the oxide convolution process.

Based on the above, it was concluded that PtAl bond coats having columnar grain structures as a result of the deposition process are not favorable for the thermal fatigue properties of a TBC. It was proposed that a different microstructure could improve TBC life.

In response to the above, a process for intentionally recrystallizing at least the surface of an aluminide bond coat was investigated for the purpose of evaluating the effect on TBC life. The investigation was directed to achieving and evaluating two effects: modification of the bond coat microstructure through controlled recrystallization to alter grain boundary structure, strength and chemistry, and modification of the bond coat surface stresses localized at grain boundaries through altering the surface grain morphology. It was postulated that the latter could be beneficial to eliminate high stress concentrations where grain boundaries create irregularities in the bond coat surface, as seen in Figure 2.

#### TRIAL #1

In a first trial, a group of specimens were coated with TBC systems that included VPA two-phase PtAl diffusion bond coats, and then evaluated by furnace cycle testing (FCT) at about 2075°F (about 1135°C) with one-hour cycles. All of the specimens underwent conventional grit blasting (80 alumina grit at 60 psi), while a limited number of the specimens were subjected to various intensity levels of zirconia bead peening, including intensity levels of about 8A (100% coverage), which is above that achievable with the dry glass bead peening (up to 6A) taught by U.S. Patent No. 4,414,249 to Ulion et al. Some of the peened specimens achieved a FCT life that was about 1.5 to 2 times greater than that of the baseline specimens (grit blasted only). A detailed examination of the best peened specimens revealed that the TBC spallation mode in these specimens was different from the typical mode shown in Figures 2 through 5. Specifically, TBC spallation occurred as a result of a relative smooth oxide delamination from the bond coat,

with grain boundary convolutions rarely being observed.

Some of the shot peened specimens exhibited overall or at least surface recrystallization of the PtAl bond coat as depicted in Figures 7 and 8, respectively, in which reference numbers are used consistent with the same features represented in Figures 2 through 5. In these fully and partially recrystallized specimens, the surfaces of the bond coats 24 at failure were smoother than that of the baseline unpeened bond coats (i.e., bond coat 24 in Figure 2), and the recrystallized grains 48 were substantially equiaxed instead of the columnar shape of the original grains (i.e., grains 32 in Figure 2). Yet other peened specimens developed triangular-shaped grains in certain regions of their bond coat surfaces, similar to the grains 42 shown in Figure 6. These specimens were concluded to have been peened at less than optimal intensities. The recrystallized bond coats were observed during examination to be single-phase as a result of the second phase having dissolved during recrystallization.

Finally, other peened specimens from the same investigation did not yield any higher level of FCT life as compared to the baseline specimens. These specimens did not exhibit bond coat recrystallization or consistent formation of triangular grains at the coating surface. Furthermore, the spallation mechanism for these specimens did not appear to be different from the typical spallation mode on the baseline samples.

From the above, it was observed that an aluminide bond coat that had undergone recrystallization to yield equiaxial grains could result in significantly improved spallation resistance (about 1.5 to 2 times improved FCT life) as compared to the aluminide bond coats that had not undergone a similar recrystallization.

Because recrystallization is dependent on peening intensity (cold working), it was concluded that a sufficient peening intensity was critical to achieving improved spallation resistance by way of the recrystallization observed for the best specimens from this trial. Consequently, peening an aluminide bond coat for the limited purpose of improving surface finish (e.g., Ulion et al.) would not result in the recrystallization effect sought by the present invention.

#### TRIAL #2

In a second trial, the surfaces of six Ni-based superalloy specimens coated by VPA with single-phase PtAl bond coats were shot peened with zirconia or stainless steel shot with an intensity of about 10A and a coverage of about 100%, followed by heat treatment at about 2050°F (about 1120°C) for one hour. The heat treatment caused recrystallization throughout the additive layers of the bond coats, though with grain growth that yielded the microstructure represented in Figure 9. It was concluded that, because these bond coats were single-phase PtAl and therefore lacked the second phase of the previously tested specimens, the fine equiaxed grain microstructure resulting from the two-phase structures (Figures 7 and 8) was not obtained. Instead, the new grains that developed extended into the original diffusion zone, thereby displacing the refractory phases from the new grain boundaries. As a result of recrystallization, the surfaces of the bond coats were "reformed," causing all original surface features to disappear. The reformed bond coat surfaces were much flatter than the as-deposited bond coat surfaces, which had grain boundary ridges characteristic of the deposition process (Figure 2). However, fine steps of about one to two micrometers were observed to form between adjacent recrystallized

grains 50.

The specimens were then coated with 7%YSZ deposited by EBPVD and tested by FCT at about 2125°F (about 1160°C) with one-hour cycles. The TBC life of the recrystallized specimens was about 300 to 320 cycles, while historically specimens of this type spall after an average of about 230 cycles. From these results, it was concluded that the peening and heat treatment parameters are sensitive to the coating type, i.e., single-phase versus two-phase aluminide bond coats. Specifically, the single-phase aluminide bond coats did not develop the equiaxial grains characteristic of two-phase aluminide bond coats and, apparently as a result, did not exhibit as great an increase in spallation resistance.

In view of the above, the present invention provides for the recrystallization aluminide bond coats to yield a grain structure capable of improving the service life of a TBC adhered to the bond coat. Recrystallization can be induced by a surface mechanical treatment that introduces cold working into the bond coat, so that a surface region or the entire bond coat undergoes recrystallization when sufficiently heated to drive the recrystallization process. Based on test results, shot peening with full surface coverage and an intensity of at least 6A is believed to be necessary. More particularly, a shot peening intensity of about 6A to 10A is believed optimal for two-phase aluminide bond coats to yield an equiaxial microstructure (Figures 7 and 8) during subsequent heat cycles. The maximum intensity of this range is established by that which the bond coat can withstand without incurring brittle fracture. In contrast, a higher shot peening intensity of about 8A to 12A is believed necessary for single-phase aluminide bond coats to yield the microstructures represented in Figures



7 through 9. The maximum intensity for this range is limited to avoid damage to the component surface and alloy properties beneath the bond coat.

The equiaxial microstructure (Figures 7 and 8) achieved with the two-phase aluminide bond coats was only occasionally observed with the single-phase aluminide bond coats after recrystallization, and it appears as a consequence that a lesser degree of improvement in spallation resistance was achieved for the single-phase bond coats. However, it is possible that an equiaxial microstructure could be more consistently achieved with a single-phase aluminide bond coat if processed with different cold working and heat treatment parameters.

While shot peening is the preferred cold working method as it can be well controlled and characterized in terms of stresses distribution, it is foreseeable that other cold working methods could be used. Furthermore, while recrystallization was caused to occur throughout the tested specimens, it is believed that the recrystallization of grains at only the aluminide bond coat surface could yield desirable results, since the spallation mechanism in an aluminide bond coat initiates and propagates from the alumina-bond coat interface.

In addition, while the recrystallization process is preferably initiated with a specific heat treatment for this purpose, recrystallization can also be accomplished during deposition of the TBC in some cases. A preferred heat treatment is believed to be a temperature of about 2000°F to about 2100°F (about 1090°C to about 1150°C) for a duration of about 0.5 to three hours. A preferred final grain size for the equiaxed grains of the recrystallized bond coat is not less than five micrometers in order to discourage aluminum loss

While the invention has been described in terms of a preferred embodiment, it is apparent that other forms could be adopted by one skilled in the art. Therefore, the scope of the invention is to be limited only by the following claims.

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